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# Synthesis of the Hydroxide Cluster $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}]^{15+}$ from an Aqueous Solution

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**ABSTRACT:** A scalable synthesis of the "flat" tridecameric inorganic cluster $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}]^{15+}$ has been realized by treating an aqueous aluminum nitrate solution with a zinc–metal powder at room temperature. Single crystals and polycrystalline samples are readily obtained in yields exceeding 55% relative to the starting reagent $Al(NO_3)_3$. Products have been characterized by X-ray diffraction and solid-state $^{27}Al$ MAS and MQMAS NMR.

Aluminum is the third most abundant element in the terrestrial environment, occurring in a wide variety of rocks and minerals. In water, the $Al^{3+}$ aqua ion hydrolyzes to produce a variety of molecular species and hydroxide phases. These phases are key elements in our understanding of aluminum in natural water systems, and they are the basis for several applications and commercial products.[1]

Although various types of inorganic polynuclear aluminum hydroxide nanoclusters have been proposed to exist in water, only a few examples have been isolated.[1,2] The known structure types are generally grouped into two distinct classes. The first class comprises structures similar to that of the $\varepsilon$ isomer of the Baker–Figgis–Keggin ion, which contains a tetrahedral $AlO_4$ core surrounded by distorted $AlO_6$ octahedra sharing edges. This class includes the ions $[Al_{12}(AlO_4)(OH)_{24}(H_2O)_{12}]^{7+}$ and $[Al_{30}O_8(OH)_{56}(H_2O)_{24}]^{18+}$.[3−6] The second class is characterized by the condensation of distorted octahedral $AlO_6$ units alone, comprising the ions $[Al_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$, $[Al_8(\mu_3\text{-}OH)_2(\mu\text{-}OH)_{12}(H_2O)_{18}]^{10+}$, and $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}]^{15+}$.[7−10] As an example of the latter category, the structure of the "flat" $Al_{13}$ cluster $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}]^{15+}$ is built around an $AlO_6$ core, which is circumscribed by six additional $AlO_6$ units through $\mu_3$-OH bridges, establishing a coplanar configuration (Figure 1). Six additional $AlO_6$ octahedra are alternately appended above and below the primary plane by sharing O vertexes (Figure 1b).

Among the reported aluminum hydroxide clusters, this "flat" $Al_{13}$ has long been an enigma. It is generally not observed in speciation studies, and reported synthetic procedures of inorganic salts suffer from very long reaction times and poor yields.[1,9] In 2008, however, Gatlin and co-workers[10] demonstrated a facile synthesis of the "flat" $Al_{13}$ cluster. In their work, a methanol solution containing dissolved $Al(NO_3)_3$ was treated with an organic nitroso-containing compound, and following evaporation of the solvent, the cluster was synthesized in yields up to 47% relative to $Al(NO_3)_3$. Unfortunately, the use of highly toxic nitroso-containing compounds hinders the large-scale production of the cluster. Herein, we introduce a green, scalable method for producing the nitrate salt $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ from an aqueous solution.

The desired hydroxo $Al_{13}$ cluster should readily form upon an increase in the pH of a simple aqueous solution of $Al(NO_3)_3(aq)$. The synthetic challenge is preventing the formation of the tetrahedral species $Al(OH)_4^-$, which can lead to nucleation of Keggin-type structures. Solution-speciation and synthetic studies in aqueous solutions have predominately been conducted via titration of an acidic $Al(NO_3)_3$ solution with a base. Such a procedure, however, favors the formation of tetrahedral species such as $Al(OH)_4^-$. We have adopted an alternative approach wherein an active metal, zinc, is used to controllably reduce the acidic nitrate solution. In this way, a gradual increase in the pH is achieved commensurate with the controlled dissolution of the zinc. Nucleation of tetrahedral species is prevented, offering a direct route to the "flat" $Al_{13}$ cluster.

The initial solution was prepared by dissolving 30.01 g of $Al(NO_3)_3\cdot 9H_2O$ (Baker Analyzed reagent, ACS grade) in Millipore water ($\rho$ = 18.2 M$\Omega\cdot$cm) to make a 50-mL solution. A total of 2.82 g of a zinc metal powder [Alfa Aesar, −140 + 325 mesh, 99.9% (metals basis)] was then added to this clear solution. The molar ratio between zinc and aluminum was 1:2. The reaction mixture was stirred overnight to ensure that the zinc powder completely dissolved. The clear solution was then filtered into a dish and placed in a fume hood for evaporation of the water. As the solution became concentrated, numerous colorless crystals began to grow, reaching sizes of several millimeters.

A crystal was physically isolated from the batch and analyzed by single-crystal X-ray diffraction methods (Bruker Apex CCD diffractometer, Mo K$\alpha$ radiation, $\lambda$ = 0.070 73 Å, $T$ = 173 K).[11] The unit-cell parameters and space group are consistent with those previously reported for $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$.[10]

Forced evaporation of the water resulted in a polycrystalline precipitate containing a mixture of the aluminum nanocluster salt, $Zn(NO_3)_2$, and unreacted $Al(NO_3)_3$. We have found that $Zn(NO_3)_2$ and $Al(NO_3)_3$ can be selectively removed by washing the product with isopropyl alcohol. The resulting powder was analyzed via powder X-ray diffraction [Rigaku Ultima-IV, Cu K$\alpha$

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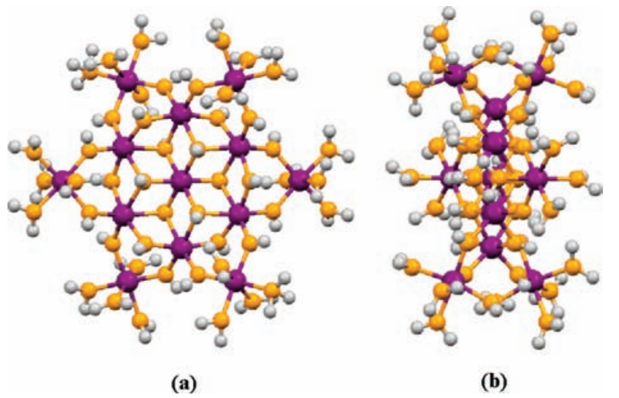

**Figure 1.** Structure of the “flat” $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}]^{15+}$ cluster: (a) perpendicular to the central plane; (b) parallel to the central plane. Color code: Al, violet spheres; O, orange spheres; H, white spheres.

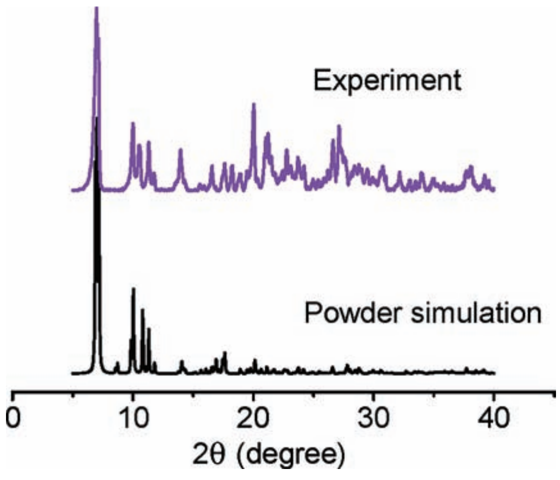

**Figure 2.** Powder X-ray diffraction pattern of the polycrystalline sample and powder simulation pattern from the single-crystal structure of $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$.

radiation, step size = 0.02° ($2\theta$)]. As seen in Figure 2, the experimental diffraction pattern agrees well with that calculated from the reported single-crystal data of $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$, confirming the synthesis of the desired compound. The yield was calculated to be 55.2% (~7.2 g/batch) on the basis of $Al(NO_3)_3$. Higher yields could likely be realized by increasing the Zn:Al ratio in the reactant mixture. At a ratio of 1:1, however, the mixture transforms into a transparent gel before all of the zinc powder dissolves. Characterization of the product phases resulting from the use of high zinc loadings is ongoing.

The product has also been analyzed with $^{27}Al$ magic-angle-spinning (MAS) solid-state NMR spectroscopy (data not shown). The measurements were conducted in a 2.5-mm HX MAS NMR probe on a Varian Inova 400 MHz NMR spectrometer. Experiments were performed at MAS rotational frequencies of 10 kHz with a $^{27}Al$ observed frequency of 104.166 MHz. Typical $\pi/2$ pulses were 1.8 $\mu s$ with recycle delays of 2 s. The $^{27}Al$ MAS spectrum reveals a set of overlapping quadrupolar-broadened resonances that arise presumably from the three types of six-coordinate aluminum sites in the cluster (Figure 1).

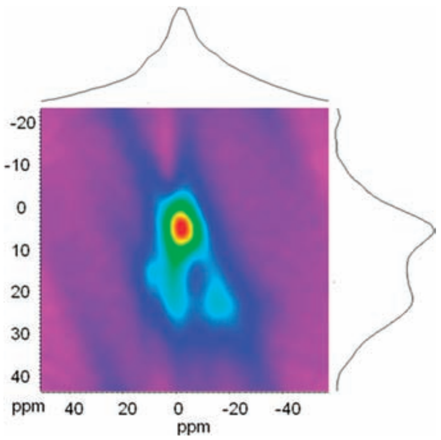

**Figure 3.** $^{27}Al$ MQMAS of $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$.

Importantly, we observe no clear indication of a four-coordinate aluminum species (based on the absence of high-frequency $^{27}Al$ chemical shifts).[12] To more closely analyze the aluminum sites, we have performed a multiple-quantum MAS (MQMAS) experiment; MQMAS is frequently applied to half-integer quadrupolar spins ($I = {}^3/_2, {}^5/_2, {}^7/_2, ...$) to resolve resonances that overlap in traditional MAS NMR because of the quadrupolar broadening of the central transition.[13,14] In the two-dimensional spectrum, the frequency is determined by the isotropic shift along one axis and by the isotropic part of the quadrupole interaction along the other. Thus, narrower lines result from each chemical species, allowing for separation of overlapping, crowded resonances. The results of this experiment are illustrated in Figure 3. The spectrum reveals the presence of three distinct aluminum sites in the powder with different quadrupolar broadening arising from variation in the electric-field gradient surrounding each site, which is consistent with the schematic of aluminum centers in the $Al_{13}$ cluster (Figure 1). Additional computational modeling will be required to make assignments of the resonances to specific sites in the cluster.

Previous efforts to examine the speciation and preparation of hydroxide clusters in aqueous $Al^{3+}$ solutions have mainly relied on titration of a solution containing aluminum with controlled amounts of a base.[3,4,15,16] This base addition generally leads to an immediate precipitation, which dissipates on stirring, or the solution is heated to 80−90 °C to limit precipitation. It is well-known that the tetrahedral species $Al(OH)_4^-$ forms at a pH as low as 7, becoming the dominant species at high pH.[17] Base titration will produce a locally high pH environment and gradient near the entering droplet, which inevitably forces the formation of $Al(OH)_4^-$. Once this tetrahedral unit forms, it will quickly condense, with six-coordinate $Al^{3+}$ aqua ions existing across the pH gradient to establish the core of a Keggin structure. Heating also favors Keggin formation through forced hydrolysis of the $Al(OH)_4^-$ unit. A similar mechanism has been proposed on the basis of $^{27}Al$ NMR analysis of an aluminum chloride solution titrated with sodium carbonate.[18]

In our work, zinc powder serves as a reducing agent, slowly consuming nitric acid generated from aluminum hydrolysis, which results in a gradual increase in the pH of the system. In the absence of a severe pH gradient toward basic conditions, the $Al^{3+}$ ions retain a six-coordinate environment associated with acidic conditions. The rising pH then forces condensation of these species to form the "flat" $Al_{13}$ cluster. We have found that the technique can be extended by using aluminum metal in place of zinc metal, but here the native oxide coating of the aluminum metal produces a byproduct that is difficult to remove from the product. In a similar way, the slow dissolution of $Al(OH)_3(s)$ in $Al(NO_3)_3(aq)$ can be used to gradually raise the pH and selectively precipitate the aluminum cluster. We note that related methods have been used to prepare sulfate salts of the clusters $[Al_2(\mu\text{-}OH)_2(H_2O)_8]^{4+}$ and $[Al_8(\mu_3\text{-}OH)_2(\mu\text{-}OH)_{12}(H_2O)_{18}]^{10+}$ by reacting excess aluminum—metal powder with sulfuric acid.[7,8]

With this strategy, we have been able to readily scale the production of $[Al_{13}(\mu_3\text{-}OH)_6(\mu\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15}$ to large quantities. Such quantities have proven useful for examining the material as the precursor to solution-processed $Al_2O_3$ and related thin films for electronics. We will describe findings from these studies in forthcoming contributions.

The synthesis also provides new insight into the speciation of $Al^{3+}$ in aqueous systems. Throughout the long history of aluminum chemistry, Keggin ions have become known as dominating species in weakly acidic aqueous environments. Our results indicate that this state of affairs may largely be a result of the method (solution-based titration) that is used to control the pH and force condensation. We have provided a reaction pathway that leads to an "uncommon" product, ostensibly under the same pH conditions, leading to formation of the Keggin ion. Hence, care should be taken in interpreting speciation studies conducted via a standard titration, especially where the coordination environment of a metal ion changes as a function of the pH. In such systems, titration can be an especially *unnatural* way to establish the metal-ion chemistry of a *natural* water system.

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(11) Crystal diffraction data: triclinic, space group $P\bar{1}$, $a = 12.877(4)$ Å, $b = 13.122(6)$ Å, $c = 13.361(10)$ Å, $\alpha = 79.86(4)°$, $\beta = 73.46(3)°$, $\gamma = 88.80(4)°$, $V = 2128(2)$ Å$^3$.

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